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RADICALS IN CHAIN REACTIONS

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- USSR -

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RADICALS IN CHAIN REACTIONS

- U S S R -

[Following is the translation of an article entitled "Radikaly V Tsepnikh Reaktsiyakh" (English version above) by V. V. Voyevodskiy and V. N. Kondrat'yev in Uspekhi Khimii (Advances in Chemistry), Vol XIX, No 6, Moscow, 1950, pages 673-696.]

Russian chemical science has always played a leading role in the field of study concerned with the velocities of chemical reactions, just as it has in many other fields. Starting with the works of A.N. Bakh, N.A. Menshutkin, N.A. Shilov, S.V. Lebedev -- pioneers in this field -- a great number of research projects by Russian and Soviet physical chemists has been devoted to the treatment of this subject. It has received an especially wide development in our country during the Soviet period, when N.N. Semenov created the theory of chain reactions, which has formed the basis of modern kinetics.

The great significance of the chain theory for chemical kinetics is becoming more and more apparent as the study of chemical reactions of various classes induces us evermore to see reactions as governed by the chain mechanism. Today we can regard as firmly established the fact that to reactions of this type belong - along with oxidizing reactions and halogenization reactions - reactions of polymerization, photochemical and pyrolitic (cracking) and, apparently, many of the catalytic reactions.

The distinguishing peculiarity of the mechanism of chain reactions is the leading role that the active centers of reaction -- free atoms and radicals -- play

therein. Due to their high chemical activity, these centers enter comparatively easily into chemical interaction with saturated molecules. And since free valency can be saturated only as a result of the interaction of two radicals (here we have in mind univalent radicals), interaction of a radical with a saturated molecule always creates a new radical which, in its own turn, enters into interaction with a saturated molecule, and so on. Periodic regeneration of radicals in the process of chemical interaction is what lies at the basis of the chain mechanism of reactions.

The above-mentioned ease of interaction of free radicals with saturated molecules, as well as the preservation of free valency in that interaction, resulting in sufficient length of chains, these constitute the reasons for the wide prevalence of chain reactions. Therefore, despite the fact that the generation of the initial active centers, which initiate chains, involves a great expenditure of energy and is, for that reason, a comparatively rare process, the speed of a chain reaction can considerably exceed the speed of a simple reaction. Let us illustrate what has been said by the following example.

Examining the thermal reaction of halogen and hydrogen, i.e. reaction $H_2 + X_2 \longrightarrow 2HX$ (X = Cl, Br or I) and assuming alongside the simple reaction

$$H_2 + X_2 = 2HX, \qquad (1)$$

a chain reaction, which proceeds in accordance with the Nernst mechanism, for the initial stage of stationary reaction -- on the assumption that the initial active centers of the chain reaction are the atoms of halogen -- we may present the summary speed of reaction in the following form:

$$w = 2k_1(H_2)(X_2) + 2k_2(H_2)\sqrt{K(X_2)},$$

where k_1 -- the constant of velocity in the simple reaction (1);
k_2 -- the constant of velocity in the process

$$X + H_2 = HX + H \qquad (2)$$

and K -- the equilibrium constant for X_2 2X. The first item in the expression for w represents the velocity of the simple (w_1), the second item -- the velocity of the chain reaction (w_2). Thus, for the interrelation of velocities of both reactions we have:

$$\frac{w_2}{w_1} = \frac{k_2}{k_1}\sqrt{\frac{K}{(X_2)}}$$

or

$$\frac{w_2}{w_1} \sim e^{\frac{E_1-E_2-\frac{1}{2}D}{RT}} = e^{\frac{E}{RT}}, \qquad (3)$$

where E_1 and E_2 are activation heats of processes (1) and (2) respectively, and D -- dissociation heat of halogen. Quantity $E = E_1-E_2-\frac{1}{2}D$ has the following values: -- 7 Kcal (I), + 7 Kcal (Br) and +21 Kcal (Cl), from which it is possible to conclude that, unlike iodine, the chain reaction in the case of bromine or chlorine, the chain reaction must have a predominant significance. Indeed, it is known from experiment that the thermal reaction of those halogens with hydrogen follows the chain mechanism, while the reaction with iodine is a simple one.

Prevalence of chain reaction over the simple one is especially likely in the case of ramified chains, whose coming into existence is, apparently always connected with the presence, in the reaction zone, of molecules with divisible bondings (e.g., oxygen molecules or molecules of an incompletely non-bonded compound, because the presence of dissociable bondings serves as a prerequisite for the possibility of elementary processes in the system -- processes which lead to an increase in the number of free valencies by two units.

The wide occurrence of chain reactions, and the tremendous role played in their mechanisms by free atoms and radicals, make the study of their chemical properties one of the principal tasks of chemical kinetics. Despite the large body of research in the field of chemistry of free radicals and atoms, and despite some successes achieved here, much remains to be done in the direction of experimental and theoretical study of specific types of elementary reactions which proceed with the participation of atoms and radicals, and also in the direction of determining the probability -- and,

therefrom, the velocity -- of reactions of that or another type, especially in terms of dependence on structure of the radical itself, as well as of the molecule reacting with it. It is precisely this solution of the task in question, which has a tremendous theoretical and practical importance, that will lend chemical kinetics such a degree of completeness as is the case with, for instance, chemical thermodynamics.

This article represents an attempt at a systematic examination of those essential data in the chemistry of free atoms and radicals which present a special interest from the view point of the chain theory of chemical reactions.

Summing up, to some extent, what has so far been achieved in this area of chemical kinetics, one can clearly see the principal paths of its further development and be in a position from which to formulate with more precision the specific problems whose solutions should hasten the resolution of the main problem.

In the course of a chain reaction the active centers participate in processes of three types: initiation, development, and disruption of chains. With this in mind, we shall divide all of the material under discussion here into three parts.

I. Genesis of Active Centers

The creation of active centers is the main condition for initiating chain reactions. Active centers are free atoms or radicals. In a great number of cases this process is connected with molecular break-up into fragments which do not possess valency-saturation. In the case of incompletely bonded compounds the creation of an active center through a partial break in complex radical-bondings without molecular fission is quite probable. This leads to the appearance of bi-valent radical (bi-radical). The mechanism of birth of a radical is either known with greater or lesser certainty, or may be comparatively readily determined, only in the case of photochemical reactions. Here the continuous absorption spectrum of chemically-active light presents a reliable criterion as to the effect that the initial photochemical act represents molecular dissociation, i.e., the breakdown of the latter into radicals, in the very same manner as the discontinued spectrum of absorption testifies to the excitation of a molecule. Furthermore, if excitation is connected with the

transition of the molecule from singlet [singletnoye] state into that of a triple spectral line, a bi-radical comes into existence as a result of the excitation.

The bi-radical character of molecules activated by light was for the first time postulated by A.N. Terenin 1/. This concept later received experimental confirmation in the numerous works of Terenin himself and his school2/, as well as in the works of other researchers.

In contrast to photochemical reactions, the mechanism of radical formation in thermal reactions allows at the present time only the construeing of more or less probable suppositions. At any temperature a certain amount of free radicals is always present in gas or liquid as a result of dissociational equilibrium. However, at temperatures below 1000°K, their concentration and the speed of their formation in the process of simple intercollision between molecules

$$RR' + M = R + R' + M \qquad (4)$$

(R and R' -- radicals; RR' and M -- molecules) are far from always sufficient enough to lend a chain reaction a measurable velocity. This, in particular, follows from the catalytic action of various impurities and solid surfaces on the speed of chain reactions, as established through numerous experiments. These experiments induce one to suppose that in the process of radicals formation the simple exchange of energy plays a subordinate [secondary] role as compared with chemical interaction.

What concerns the formation of radicals by way of the simple thermal dissociation of molecules according to formula (4) is that the process at low temperatures is apparently, valid only in case of such comparatively short lived compounds as ozone or some of the peroxides. Specifically, the well known catalytic action of peroxides is usually connected with the facility of their dissociation upon radicals of the RO type; the dissociation here being conditioned by the low durability of connection O - O. However, little is yet known about the dissociation of peroxides. The fact that hydrogen peroxide decomposes exclusively on hard surfaces even at a temperature of 175°,3 makes the assumption, about the heterogenous-catalytic decomposition of other peroxides as well, not improbable. Further, data demonstrating the effect of solvent upon the

kinetics of decomposition of peroxides is available. Thus, for instance, according to findings by a number of authors 4/, benzoil peroxide decomposes at a different rate in different solvents, whereby the dependence of the rate constant on temperature, and consequently, also the energy of activation in various solvents, proves to be different. This data shows that in the thermal dissociation of peroxides -- just as in other processes of birth of radicals -- a substantial part is played by chemical factors.

Let us also note that, apparently, the fact frequently discovered by Emanuel 5/, of the existence of two forms of acyllic hydroperoxides, distinguishable by their chemical activity and mutually transformable one into another, has a close relation to the problem of decomposition mechanism of peroxides. According to Emanuel, the more active form of hydroperoxide is distinguishable from the less active one by the presence of intermolecular hydrogen bondings in the first.

Chemical interaction which leads to the birth of radicals can be presented in the most general form by means of the following elementary processes:

$$M+M' = R+R' \qquad (5)$$

and

$$R_0+M = R+M'' \qquad (6)$$

where R and R' radicals; R_0 an inactive radical or molecule possessing the properties of a radical; M,M' and M'' -- saturated molecules.

Process (5) is, apparently, most frequently realized in the presence of oxygen. Thus, for instance, it can be assumed that the birth of radicals in detonating gas is connected with the process

$$H_2+O_2 = 2OH$$

which is the most advantageous with respect to energy. However, we must regard as a more general mechanism of the formation of radicals with the participation of oxygen, the mechanism expressed by the process:

$$RH+O_2 = R+HO_2 \qquad (7)$$

Energy of activation of this process, apparently, differs little from its thermal effect, which may be estimated as 40-50 kilogram-calories. Therefore, the rate of

process (7) must considerably exceed the rateof any given process connected with simple dissociation of the molecule, i.e., with a disruption of bonds usually requiring an energy expenditure of 60, 70 kilogram-calories, and more.

The initiating role of oxygen becomes obvious when comparison is made between temperature conditions in the course of pyrolisis processes and the slow oxidation of one and the same compound. And indeed, while pyrolitic reactions proceed at a measurable rate only at temperatures of 500° and higher, the oxidizing reactions can -- as a rule -- be readily realized even at 300°. Further, one can point to the catalytic action of oxygen in the processes of oxygen cracking, in which additions of oxygen considerably hasten the process.

Proof of the appearance of free radicals occurring during interaction with oxygen lies in experiments for study of thermal disintegration of the compounds CH_3CHO and CD_3CDO[6]. Carrying out the process under extremely pure conditions, without the least trace of admixture (especially oxygen), we find that its rate is not great (t = 500°C) and the final product is the mixture $CO+CH_4+CD_4$ mixed deuteromethanes are absent. But when the reaction is conducted in the presence of traces of oxygen, its rate increases sharply; and in the reaction products we obtain a balanced mixture of all deuteromethanes. These experiments demonstrate that a temperature of 500° is insufficient to produce a disintegration of acetaldehyde into radicals, and that therefore the reaction $CH_3CHO = CH_4+CO$ proceeds along the lines of the mechanism of simple reactions, and very slowly at that. Exchange of deuterium does not occur. But in the presence of oxygen (or of other active admixtures) free radicals can be formed at the same temperature; the process follows the chain pattern, i.e., considerably faster, and since free radicals can very readily exchange atoms H and D with surrounding molecules -- mixed deuteromethanes are formed as a result of the process.

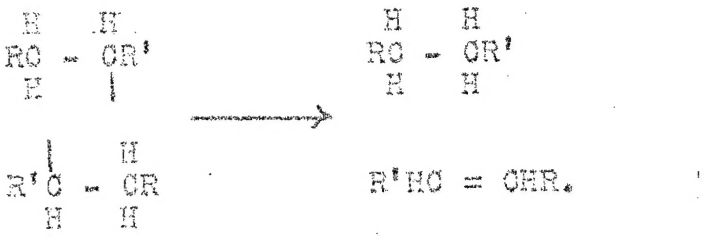
Experiments just described are in fair agreement with findings of Shtern and Polyak 7/, concerned with the study of slow thermal oxidation of propylene and propane. These authors came to the conclusion that the possibility of chain process of oxidation of those hydrocarbons at temperatures as low as 300-400° is conditioned specifically by the circumstance that the formation of initial radicals in the mixture $RH+O_2$ is

noticeably facilitated thanks to reaction (7).

The same authors point out that as temperature is increased, even in mixtures with a large amount of O_2, the process of pyrolisis dominates over oxidation. Thus, it is natural that even small additions of oxygen can sharply hasten the cracking process.

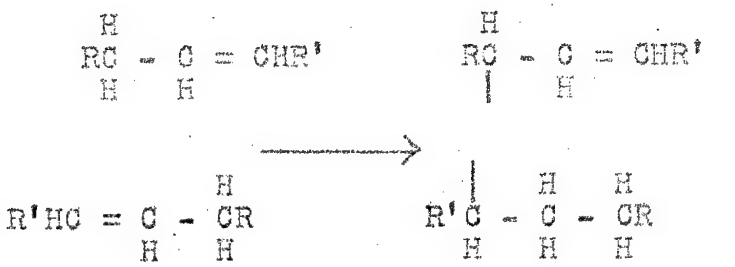
Available are also indications of the great role of traces of oxygen in the initiation of chain reaction of water-gas conversion 8/.

However, process (5) can also play a substantial part as a source of the homogenous initiation of radicals even in the case of chain reactions proceeding without the participation of oxygen. In particular, the possibility, that the birth of radicals in thermal polymerization of pure substances is conditioned by precisely this process, is not excluded. Research into kinetics and the mechanism of thermal polymerization leads us to the conclusion that the abrupt termination of polymeric chains occurs most often as a result of processes of disproportionation (see below, part III), which can be depicted by means of the following general sketch:



Here the cause of the disappearance of two radicals, leading to the disruption of two polymeric chains is the removal of an atom H from one radical to another. The low energy of activation of disproportionation processes, usually amounting to only a few kilogram-calories, indicates the facility of this transfer 9/. Therefore it should be expected that the reversed transfer of atom H from one molecule to another, i.e., the birth of two radicals from interaction of molecules, should occur with a significant probability, and the ativation energy of this process must be close to the heat of the reaction and approximately equal to the difference between the energies of connections C=C and C - C (~40 kilogram-calories). Thus, for instance, the birth of radicals in thermal polymerization of pure hydrocarbons of the ethylene series can be expressed through the following

process:



Competing with this process is, apparently, this process:

which leads to the birth of a bi-radical.

As examples of molecules with a lesser or greater extent of radical properties there may serve the molecules NO and NO_2. Specially, not excluded is the possibility that catalytic action of nitrogen dioxide in reactions of slow oxidation of hydrocarbons is conditioned by the process

$$RH+NO_2 = R+HNO_2$$

which represents an illustration of process (6). The binding energy of atom H in a molecule of nitric acid, equalling several tens of kilogram-calories, gives a energy gain as compared with the simple disintegration of the RH molecule into R and H, as a result of which radicals R in the presence of NO_2 are formed with great ease.

All of the foregoing concerning birth of radicals pertains in equal degree to reactions occurring in both gaseous and liquid phases. Special conditions favorable for the birth of radicals are to be found in solutions of electrolytes. The specifics of this process in the ionized medium of the electrolyte is conditioned by the participation of ions in it and by the readiness of transfer on the part of the electron from one particle to another. Dissociation of a molecule with the participation of the electron, leading to the

formation of a free radical, is well-known for the gaseous phase, where this process -- in the case of slow electrons 10/ -- runs its course as follows:

$$e + RX = R + X^- \qquad (8)$$

Here X stands for the electronegative atom or radical. Polyvalent ions often serve as source of electrons in solutions. Their presence does, in particular, condition the catalytic action of salts. Thus, for instance, according to a fairly widespread conception, at the base of the chain reaction of catalytic decomposition of hydrogen peroxide by salts of iron lies the process11/

$$Fe^{\cdot\cdot} + H_2O_2 = Fe^{\cdot\cdot\cdot} + OH' + OH,$$

analogous to the process (8). Let us further indicate that, according to Haber and Willstätter 12/ the birth of radicals in organic reactions in general, in enzymatic reactions in particular, materializes in accordance with the following general mechanism:

$$RH + Me^{\cdot\cdot\cdot} = R + H' + Me^{\cdot\cdot} \qquad (9)$$

The initiating action of surfaces also plays a very important role in the kinetics of chain reactions. The possibility of the genesis of radicals on the surface with their subsequent flight into volume is most clearly demonstrated through Polyakov's experiments 13/. He showed that hydrogen activated by palladium possesses all the properties of atomic hydrogen and, in particular, is capable of initiating a chain reaction of oxidation. Also indicative, in that sense, is the known experiment of Haber and Alyea 14/ with crossed jets of hydrogen and oxygen, both heated in advance. In the conditions of this experiment ignition occurred only when a quartz rod was introduced at the spot where the jest crossed. However, it must be noted that this experiment permits a dual interpretation, because the possibility of explaining the igniting action of the rod in terms of aerodynamic factors (compression of gases when the jet hits the surface of the rod) is not excluded. The initiating action of surfaces in the role of catalyst was quite convincingly demonstrated in the experiments by Koval'skiy 15/. Measuring the distribution of temperature along the radius of a cylindrical container of

reaction, under the conditions of a catalytic reactions in process, (the catalyst was applied to a thin rod placed upon the axis of the container of reaction, or directly upon the inner surface of the container), Koval'sky found that in a number of reactions (H_2+O_2, CH_4+O_2, $C_2H_5+O_2$ and others) the greater part of heat was educed within the volume of the container. From this follows the unavoidable conclusion that the role of the heterogenous catalyst in the case of those reactions is reduced to merely generating active centers, which then enter the volume from the surface of the catalyst and stimulate a homogenous chain reaction.

The clarification of the mechanism of the birth of radicals on hard surfaces must apparently be approached also from the chemical view point, postulated earlier in this article. The prevalent role of chemical factors in the process of catalytic action of surfaces is obvious from the exceptional specificity of catalytic processes. Examining the activating action of surfaces as a result of chemical interaction between the activated substance and the catalyst, it is not difficult to show that the birth of the radical on the surfaces must be thermodynamically more advantageous as compared to simple dissociation of a molecule into radicals. Indeed, presenting the summary process of heterogenous-catalytic birth of the radical in the form of equation

$$RR' + K = R+R'K \qquad (10)$$

(K -- catalyst; R'K chemisorption product of radical R'), we see that process (10) gives a gain in energy (equal to the quantity of energy educed in the formation of exothermic compound R'K) as compared to process (4). Let us note that the chemical nature of process (10) is close to the homogenous-catalytic process of type(7).

Processes (1) and (7) also have a common aspect; owing to the preservation of even-numbered valency in the reacting system, two free valencies spring up as a result of each of these processes. In the case of the homogenous process (7) both valencies belong to two radicals (R and HO_2); while in the case of the heterogenous process -- to the volume-entering radical R and to the chemisorbed radical R'. Thus, as a result of process (10), the surface of the catalyst obtains new properties, which have a substantial significance in the kinetics of heterogeneous-catalytic reactions. In

particular, the possibility is not excluded, that, as observed in a number of cases, the increase in the activity of a catalyst in the process of an occurring reaction conditioned, to some extent, by precisely such alteration of its surface.

II. Development of Chains

Active centers -- free atoms and radicals, having sprung into existence by one way or another in a given chemical system, -- are the initiators of chains, the length of which is determined by conditions of the reaction in process. In the case of non-ramified chain reactions, the development of chains is conditioned by the process of the following type

$$R + X = R' + X', \qquad (11)$$

which lies at the base of the chain mechanism of the majority of reactions (in particular, reactions of halogenation and pyrolisis), or by the process of type

$$R + M = MR, \qquad (12)$$

which lies at the base of the mechanism of a large group of reactions of polymerization and is also one of the basic processes in slow oxidation reactions. For the latter case we have used the letter M to designate the oxygen molecule.

Process (12) is obviously possible only when the molecule M has divisible number of connections (such as, in particular, O_2 molecules, molecules of olefins, etc), because only under this condition is the formation of the MR radical possible.

Thus, primary radicals, entering into a reaction, create new radicals -- the secondary ones. The latter, in their own turn, go through a chemical transformation, and so on. As result of that, a certain amount of various radicals is formed in the reacting mixture; the variety of those radicals being determined by the degree of complexity of the chemical mechanism of the reaction. Among all the radicals, bi-valent radicals occupy a special place -- their interaction with saturated molecules produces two univalent radicals each time. The

appearance of bi-valent radicals is always connected with an increase in the number of free valencies, which is the basic requirement for the branching out of chains. So in the presence of molecular oxygen the number of free valencies increases as result of the fission of molecule O_2 when interacting with a univalent radical:

$$R + O_2 = RO+O \qquad (13)$$

Detection of oxygen atoms in various flames 16/ may be viewed as proof that process (13) actually occurs in burning reactions. The oxygen atom thereby coming into existence, interacts with the molecule of the fuel

$$O + RH = R+OH \qquad (14)$$

as result of which there is formed a hydroxyl and a second radical, also univalent. Summing up processes (13) and (14), we obtain the following brutto-equation

$$R + O_2 + RH = RO + OH + R.$$

Thus, as result of these processes, alongside the regeneration of radical R, there emerge two new radicals, which leads to the ramification of the chain.

Process (13) has the greatest rate in cases where the univalent radical is represented by atom H, which is associated with a comparatively low activation energy of reaction $H+O_2 = OH+H$ (18 Kcal), conditioned by a greater energy of connection of atoms H and O. Already at a temperature of 400-500° this reaction has a considerable speed, which follows from the possibility of realizing the burning of hydrogen at these temperatures 17/.

In the case of other univalent radicals, owing to a lower energy of connection R-O (as compared to H-O), process (13) becomes highly endothermic and therefore must have a noticeable speed only at temperatures considerably higher than 500°.

Indeed, in the case of hydrocarbon radicals, for instance, since the bond energy C-O amounts to 70-80 kilogram-calories, activation energy for process (13) emerges as a quantity of $\sim$50 kilogram-calories. Hence, for the probability of this process, i.e., for the relation of an effective number of collisions $R+O_2$

to the full number of collisions at 500°, there emerges a quantity smaller than 10^{-14}. Because of this, it is not very probable that in the slow oxidation of hydrocarbons, i.e., in a reaction proceeding at 300-400°, atoms of oxygen could spring up in any perceptibly appreciable quantities. Therefore, if in reactions of burning, occurring at a sufficiently high temperature, process (13) may be regarded as the basic ramifying process, then the ramification mechanism in low-temperature reactions of slow oxidation must be different.

Ramifications [branching off] may also be associated with such exothermic processes, the energy of which transforms itself into chemical energy of newly-formed free atoms or radicals. It is highly probable that ramifications in the reactions of burning of the dry carbon dioxide in oxygen is conditioned by the following process:

$$O + CO + O_2 = CO_2 + 2O + 8{,}1 \text{ kg-cal.}$$

The presence of ramifications in reactions of slow oxidation of hydrocarbons is brought out by a number of facts pertaining to the phenomenology of these reactions. First of all, their speed during the initial time-stage conforms to the law e^{kt}, which is reflected in the S-shaped form of the kinetic curve in the presence of a more or less sharply pronounced induction period. Further, in the case of these reactions, observable are maximal phenomena characteristic of ramified chain reactions, which, in particular, find expression in the existence of sharply defined areas of cold-flame burning, as well as in the fact that the reaction of slow oxidation usually terminates way before the reagents are totally spent. It was also established in some cases that rate of a reaction changed sharply with change in the diameter of reaction container or when pressure was changed in a container with a constant diameter 18/ However, the slow speed of slow oxidation reaction leads us to the conclusion that these reactions conform to a chain mechanism which is different from the usual mechanism of ramified chain reactions. According to Semenov 19/ -- "the basic chain in these cases develops with an unusual speed (i.e., very rapid) and is not accompanied by ramifications in the sense usually accepted by us." However, "as result of reaction in

this primary chain there is formed not the final, but some intermediate, relatively durable, product of reaction. This intermediate product, accumulating in the basic gas, begins itself subsequently to react in an independent manner, supplying end-products. However, infrequently and at the expense of the energy of this secondary reaction, centers are created capable of starting anew the chain of the primary reaction". Those secondary chains of Semenov he calls "chains of degenerated ramification."

Characteristic peculiarity of the reaction of slow oxidation of hydrocarbons lies exactly in the wide variety of products of the intermediate type, which are formed in the course of reaction alongside the end-products of oxidation CO, CO_2, H_2O. With the secondary reactions of any one of those intermediate products can namely be connected the degenerated ramifications.

The possibility of the radiation, in reactions of slow oxidation, of the considerable energy necessary for the creation of secondary active centers, emerging through the mechanism of degenerated ramification, follows directly from data of the spectral analysis of cold flames. According to these findings, approximately 80 kilogram-calories are educed within the cold flame in the form of electronic radiation energy, and the sole carrier of the spectrum of that radiation, in the case of the cold flame hydrocarbons and of other organic matter (aldehydes, ether), is the excited molecule of formaldehyde. The fact, that the energy of excitation of formaldehyde (76 kg-cals) is very close to the difference of the bond energies for C=O and C-O(70 kg-calories) makes quite possible the supposition that the excitation of the molecule HCHO is connected with its transformation into the bi-radical H_2C-O. In favor of this supposition we have the proximity of the frequency of the valental fluctuations $H_2C \leftrightarrow O$(1187 cm^{-1}) aroused by the molecule of formaldehyde, to the frequency of the valental fluctuation of the molecule of methylalcohol (1030 cm^{-1})*.

* The frequency of the dually bonding C=O amounts to ~1720 cm^{-1}. In particular, the valency fluctuation $H_2C \leftrightarrow O$ in a normal molecule of HCHO has a frequency equalling 1744 cm^{-1}.

That fact that the excitation of the molecule HCHO is connected precisely with the group >C=O, follows also from the near coincidence of the regions of absorption (~3500 Å) in all of the aldehydes and ketones. Finally, cooparatively small values of the absorption coefficients of those substances in the indicated regions of the spectrum points to a low probability of corresponding transformations, which can be interpreted as an indication of the triplet character of the electronic level of the aroused molecule.

If therefore the supposition about the bi-radical structure of the excited molecule of formaldehyde can be regarded as to some extent substantiated, then from this we must make the subsequent conclusion that the excitation of formaldehyde occurs at the moment of its formation. Independently from the above-stated considerations, the conclusion about the impossibility of the excitation of the already formed molecule HCHO or, that molecule of HCHO which is formed from some more complex molecule (or radical), containing a ready group >C=O derives also from the fact that in the case of formaldehyde itself no cold flame is observed. Consequently, we must conclude that the aroused molecule of formaldehyde is formed as a result of direct interaction of some given atom of carbon with oxygen. The carbon here is connected only with atoms H and C. As far as the specific chemical mechanism of this interaction is concerned, for the uni-term solution of this problem at the present time we do not have at our disposal the necessary experimental data. It is possible, however, that the known point of departure here is represented by the following fact established by Stern and Polyak 7/. These authors, by the method of introducing various admixtures into the mixture of propylene and oxygen, have discovered that acetaldehyde plays an exceptionally important role as a positive catalyst of the reaction of slow oxidation of propylene, (and also of propane). From there, they had arrived at the conclusion that the ramifications generated in this reaction must be connected with the presence of CH_3CHO. In view of the fact that acetaldehyde in larger or smaller quantities is formed in many organic oxidizing reactions, it can be viewed as one of the basic substances which condition the ramifications of chains. It may be assumed that the radicals CH_3CO, which spring up as a result of the splitting off of one atom H from molecule

CH_3CHO (e.g., as a result of the process $CH_3CHO + O_2 = CH_3CO + HO_2$), or radicals CH_3, which are formed through disintegration of CH_3CO and are precisely those radicals whose direct interaction with molecular oxygen leads to the formation of an aroused molecule of formaldehyde;

$$CH_3CO + O_2 = HCHO^* + CO + OH$$

or

$$CH_3 + O_2 = HCHO^* + OH \quad *$$

As a result of these processes there emerge, instead of one disappearing radical, the new radical OH and bi-radical H_2C-O, which does lead to the possibility of the ramification of chains.

The ramification, conditioned by the participation in the reaction of bi-radical H_2C-O or of some other bi radical, e.g., $HRC-CR'H$, may be presented by the following process

$$HRC-CR'H + R''H = RH_2C-CR'H + R''. \qquad (15)$$

Processes of type (15) may have substantial significance in reactions of cracking and of polymerization.

As was already noted, the ramifications in reactions of the slow oxidation of organic substances play merely a secondary part. The fundamental significance in the mechanism of these reactions belongs in the processes connected with the development of simple non-ramified chains.

These processes are represented by processes of the type (11) and (12). In this connection process (11) must be characteristic for the reactions of various radicals with the molecule of the fuel or with molecules of stable intermediate substances which spring up in the course of oxidation. The low energy of activation, which is the property of exchange-reactions of radicals, guarantees great speed of the process (11). Process(12) plays the basic role in the interaction of radicals with molecular oxygen, thus essentially representing the

*Elbe and Lewis 20/, on the basis of considerations of energy, regard the first of these processes as the source of the aroused formaldehyde.

first stage of oxidation. The constant of speed of this process (k) can be presented as

$$k = k_2 \frac{\tau}{\tau + \tau_p}, \qquad (16)$$

where k_2 is the constant of the speed of the formation of the quasi-molecule RO_2 when R and O_2 go through a mutual collision; τ is the average span of the life of the quasi-molecule, determinable by the probability of its self-induced disintegration, into R and O_2; τ_p — average time span between two stabilising and coinciding collisions of the quasi-molecule with any other molecule. The quantity of τ_p is apparently in reverse proportion to the general pressure p.

Expression (16) gives the following maximal values of the constant k;

$k = k_2 \frac{\tau}{\tau_p}$ and $k = k_2$, which occur correspondingly at $\tau \ll \tau_p$ and at $\tau \gg \tau_p$. The first of these maximal values is obtained at low pressures or in the case of quasi-molecules formed from atoms or from simple radicals. In this case time τ differs little from the average duration of the double coinciding collision, i.e., it has the magnitude of the order 10^{-12} seconds, and because at pressures of the order of one atmosphere and at temperatures of several hundred degrees the time τ_p amounts to 10^{-9} seconds, we have $\frac{\tau}{\tau_p} \simeq 10^{-3}$. Thus, in this case ($\tau \ll \tau_p$), the constant k turns out as proportional to pressure, and process (12) is trimolecular. A well-studied example 17/ of such a process is the formation of radical HO_2 from H and O_2.

As the number of atoms increases in the quasi-molecule the time τ grows owing to the increase of the number of vibrational degrees of freedom, which secure a great facility of energy distribution within the quasi-molecule. In the case of a sufficiently complex quasi-molecule τ may significantly exceed τ_p and the constant k will become practically equal to the bi-molecular constant k_2. Process (12) in the case of the majority of organic radicals conforms apparently to the bi-molecular law.

The radical RO_2, which comes into existence in the process (12), enters into chemical interaction as per scheme (11); with other molecules, in the first place with the molecule of the original fuel, as a

result of which peroxide is formed and also a new radical-hydroperoxide in the case of the reaction

$$RO_2 + R'H = ROOH + R' \qquad (17)$$

and di-peroxide -- in the case of the reaction

$$RO_2 + R'R'' = ROOR' + R''. \qquad (18)$$

However, it must be noted that process (18) is apparently materialized with a significantly smaller probability than process (17) which, in particular, can be judged when processes (17 and 18) are compared with analogous processes.

$$R + R'H = RH + R' \qquad (19)$$

and

$$R + R'R'' = RR' + R''. \qquad (20)$$

Thus, for instance, Akeroyd and Norrish 21/ have found that the photochemical decomposition of formaldehyde, acetaldehyde and acetone at high temperatures conforms to the chain mechanism only in the case of aldehydes. The absence of chains in the photolysis of acetone must apparently be connected with the low probability of the process

$$CH_3 + CH_3COCH_3 = C_2H_6 + CH_3CO.$$

Indeed, precisely in a number of studies dedicated to the investigation of reaction in the mixture $D + D_2 + CH_3R$ at low temperatures, it is observed that methane, detected in the reaction products, is deuterated from 70-90% 22/. Inasmuch as at these temperatures CH_4, in the presence of atoms of D is not deuterated, this result points to the low velocity of the process:

$$D + CH_3R = CH_3D + R.$$

The scheme which was offered for the primary stage of the reaction of slow oxidation is confirmed through numerous observations, according to which the peroxide is indeed the main product at the first stage of oxidation of organic substances 23/, 24/.

As far as the subsequent fate of the initially-forming peroxide is concerned, in view of the infrequent ramifications of their further transformation in the

case of low-molecular hydrocarbons, a characteristic for reactions of slow oxidation, it must in the main lie in the fission into saturated molecules, which form themselves either as a result of self-induced disintegration of the peroxide or as a result of its interaction with molecules of the initial substance or of any intermediate substance.

As was shown by Ivanof 23/, when the photochemical oxidation of high-molecular hydrocarbons occurs, there are formed quite stable peroxides capable of further oxidation with the formation of biatomic peroxides. The fission of peroxides as well as the further oxidation of substances formed in this process produces aldehydes alcohols, acids, H_2O, CO, CO_2, etc. -- the whole scale of highly varied products of the slow oxidation of organic matter.

The formation of peroxides apparently does not represent the sole method of transformation of radical RO_2. Another possible avenue -- the disintegration of this radical to the point of its transformation into peroxide-- cannot be regarded as excluded, especially if we take into consideration the increased energy store of the quasi-molecule RO_2. As a result of the disintegration of the latter or of the stabilized radical RO_2 formed from it there comes into existence a new radical and a saturated molecule. It is possible that the formation of aldehydes at various points of reaction, as observable in a number of cases, is connected with the very direct disintegration of RO_2 or $R.O_2$. The above stated reaction of radical CH_3CO with molecule O_2 -- is one of the probable schemes of ramification of chains -- may also be regarded as an example of such a sort of disintegration of the quasi-molecule $CH_3CO.O_2$.

It is especially interesting to note here the the possibility of a change of the direction of the reaction by the method of adding substances which readily give up atom H. Thus, for instance, in the oxidation of hydrocarbons (C_2H_6, C_3H_3 and others) at low temperatures there apparently dominates the disintegration of radical RO_2, which leads to the break up of the skeleton and the emergence of comparatively small molecules of oxygen containing products, (HCHO, CH_3OH, CH_3CHO and others). But in the presence of HBr the radical RO_2 apparently does not disintegrate but easily transforms

itself into hydroperoxide, forming atoms of Br which regenerates the radical R and the molecule HBr as per reaction 25/

$$Br + RH = R + HBr$$

Therefore, in the presence of HBr in the capacity of stable intermediate products of oxidation we get not HCHO, CH_3CHO, etc., but a higher-molecular oxygen-containing compound (e.g., acetone in the oxidation of propane).

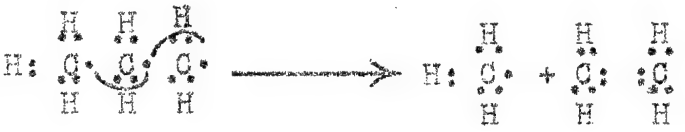
One should not think that such a dualism in properties, namely, the possibility of an entering into reaction of the inter-exchange type (17) and of disintegration, is characteristic only for radicals containing oxygen. The same dual tendencies manifest themselves quite distinctly also in the case of free hydrocarbon radicals which are formed in the course of various complex reactions (oxidation, cracking, halogenation), the dissociation of metal alkyls, etc.

Free radicals with the largest number of carbon atoms (CH_3, C_2H_5) possess a very great reaction capability in the sense that they can very easily enter into reactions with other molecules 26/. Their average life-span is therefore quite small (of the order of 10^{-3} seconds). For more complex radicals the life-span also proves to be small, but it is determined by a different cause -- not the reaction capability in the common sense of the word but by the low stability with respect to disintegration. Thus, for instance, it was shwon by direct experiments 27/ that the radical $CH_3-CH_2-CH_2-$ already at a temperature of 400° disintegrates extremely readily into CH_3 and C_2H_4. The activation energy of disintegration equals 19 kilogram-calories.

In the case of higher-molecular radicals of such types the speed of disintegration increases even more, which correspondingly leads to a diminuition of the average life-span.

Such a substantial distinction in the chemical properties of various radicals of one of the same homological series can be connected with the varied character of the interaction of the free valency electron with the remaining electrons and nuclei of the radical. In small radicals this electron is sufficiently mobile and therefore its external activity predominates, it strives

to form a pair with the electrons of atoms of those molecules with which the given radical collides. As a result of such behavior on the part of the valency electron we find the great reactiveness of these particles. In higher-molecular radicals the electron, under the influence of the remaining electrons and nuclei, is drawn inward within the radical itself and its outward activity decreases. In this it can facilitate the self-induced disintegration of the radical. This process of disintegration can be schematically presented in the following manner:



(21)

The strong interaction of the valency electron with the remaining particles in the radical does not always lead to the disintegration of the latter. In some cases, e.g., in the presence in the radical of double bonds or of a system of conjugated double bonds [sopryazhennye dvoynye sbyazi], such an interaction leads, on the contrary, to a stabilization of the radical 28/. For an example, we can compare n-propylic and aluminum radicals:

$$-CH_2-CH_2-CH_3 \quad \text{and} \quad -Ch_2-CH = CH_2.$$

While the n-propyl has a tendency towards self-induced disintegration, it is known, that allyl is rather a stable and low-activity radical.* We can judge this, if need be, by the fact that propylene exerts a considerably greater breaking influence on a number of complex reactions (of disintegration and oxidation), than, for example, isobutane. This can be partly connected with the greater inertial property of the allyl radical (Cf. part three).

Similarly to the determining of the character of hydrocarbon oxidation through the chemical properties of radicals of the RO_2 type, the above-described mechanism of disintegration of hydrocarbon radicals (21) allows

* See 26/, page 316.

us to explain a number of peculiarities of the homogeneous pyrolysis (cracking) of hydrocarbons at high temperatures 30/. According to modern concepts, cracking is a chain process. Without stopping here to discuss various proofs for this proposition and without stopping here to deal with the character of various reactions of chain genesis (Cf. part one), let us merely note that according to this theory the basic process, leading to the breaking of the C-C bond in the hydrocarbon skeleton, is the disintegration of the radical through a process of the (21) type. The cracking process may be schematically described in the following manner.

Under the influence of some external action (radical, free atom, irradiation, homogeneous catalyst) one of the least firmly connected H atoms breaks off from the molecule RH. Radical R, thus formed, disintegrates in accordance with reaction (21), forming an olefine molecule and a new radical R'. If this radical also possesses a low stability, it disintegrates further, etc.

In order to explain the composition of products of vapor-phase cracking it is also assumed 31/ that the radical of type

$$-CH_2-CH_2-CH_2- \cdots -CH_2$$

can regroup itself by means of the transfer of one of the hydrogen atoms with the formation of a more stable radical, e.g.:

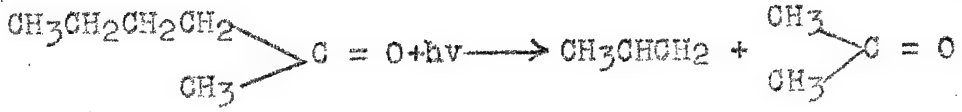
$$CH_3-CH_2-CH-CH_2-\cdots -CH_2.$$

Such transfers are strongly facilitated by the fragmented form of the skeleton of the hydrocarbon molecule. It appears most probable from geometric considerations that such transfers must occur most readily in a β- position (i.e., through one atom of carbon). Detailed findings which would permit the determination of the true mechanism of such regroupings are as yet unavailable.

The results of research into end products in the photolysis of ketones 32/ may serve as arguments in favor of the supposition stated here.

$$\begin{matrix} CH_3CH_2CH_2 \\ CH_3CH_2CH_2 \end{matrix}\!\!>\!C=O + h\nu \longrightarrow 2C_2H_4 + \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C=O$$

and



and in the case of electrochemical synthesis of olefine from partially deuterized acids 33/

$$CD_3\text{-}CH_2\text{-}COOH \longrightarrow CD_2 = CH_2,\quad CH_3\text{-}CD_2\text{-}COOH \longrightarrow CH_2 = CD_2\ ;$$

$$CD_3\text{-}CH_2\text{-}CH_2\text{-}COOH \longrightarrow CD_3\text{-}CH = CH_2\ ;$$

$$CH_3\text{-}CH_2\text{-}CD_2\text{-}COOH \longrightarrow CH_3\text{-}CH = CD_2,$$

which can be most simply explained especially with the aid of such a transfer of one atom of hydrogen.

The disintegration of a radical as described by us, which explains the appearance of olefine of low-molecular weight, does not however represent a chain process.

It can be seen from the above stated that the multi-stage disintegration of the initially-formed radical R will continue to be realized, until a sufficiently stable radical of low-molecular weight R- is formed, for which the probability of disintegration will be smaller than the probability of interaction with one of the molecules of substance that has not been subjected to completed reaction. Such a reaction which can be described in the form

$$R' + RH = R'H + R \qquad (22)$$

and will namely represent the continuation of the chain. As the result of it, the heavy radical R will be formed again, and it, in its own turn, may be subjected to re-peated dissociation resulting in the formation of a certain number of molecules of unsaturated hydrocarbons and of the radical type R', capable of entering again into reaction of chain propegation. Let us also note that saturated hydrocarbons being formed in the course of such processes must posses a comparatively small molecular weight, (CH_4, C_2H_6).

Inasmuch as the genesis of chains represents the most gradual and slowest process in the chain reaction of thermal cracking, it is absolutely clear that the in-crease of speed of this process (e.g., at the expense

of various irradiations and additions) will permit the carrying out cracking at considerably lower temperatures. Cracking of hydrocarbons and of their derivations can be induced through irradiation or adding of substances which readily disintegrate into radicals. This can be done at temperatures of the order of 200°, while thermal cracking usually proceeds at temperatures of 500-600° and higher 34/.

When comparing the cracking velocities of two hydrocarbons one should, of course, take into consideration the speeds of all three basic processes -- the origin of chains, the disintegration of the radical (21) and the reaction of chain propagation (22).

Since it is usually accepted that the origin of a chain in pure hydrocarbons occurs at the rupture of the bond C-C, for the not very light molecules (with a number of atoms C in excess of 3-4), the rate of formation can be regarded as more or less identical*. On the basis of this proposition, certain conclusions about the speed of the process can be drawn in a number of cases. This is to be done through consideration of the structure of reacting molecules. For the sake of an example, let us compare of butane and isobutane under identical conditions.*

Process $R' + RH = R'H + R$ (where R' represents radical CH_3) will proceed faster in isobutane, because the bonding of the tertiary atom H is some 4.5 kilogram-calories lower than that of the secondary 29/. On the other hand, radical $CH_3-\dot{C}H-CH_2-CH_3$ should disintegrate more readily into propylene and CH_3 than radical $(CH_3)_3\dot{C}$ -- for which the sole way of disintegration into $(CH_3)_2C=CH_2+H$ requires considerably more energy. Therefore, it is to be expected that isobutane is subjected to cracking at a lower rate than normal butane. This is confirmed by experimental data 35/ On the other hand, such difficulty does not exist when we compare the cracking of pentane and isopentane, because the radical $(CH_3)_2\dot{C}-CH_2-CH_3$ disintegrates into $(CH_3)_2C=CH_2$ and CH_3 with approximately the same rate as the normal pentyl radical. Therefore we are justified in our expectation that in this case the rate of cracking of isoparaffin

*Not excluded is also the possibility of a chain originating as a result of a rupture of one of the bonds C-H. This does not affect the validity of all of our subsequent considerations.

will be higher than that of normal paraffin. This deduction is also confirmed through experiment 36/.

Now let us examine the catalytic cracking of hydrocarbons, with the aim of determining possible common traits of reactions of this calss and of the processes of homogenous pyrolysis, and to clarify the possibilities of its occurrence along the lines of radical chain mechanism.

It is known that heterogenous cracking of hydrocarbons proceeds, depending on the properties of the catalyst, in two ways -- radically and ionically. The first mechanism is characteristic for catalysts of the type of activated coal, the second -- for the ionic catalysts of the alumo-silicate type. When activated coal is employed, one of the hydrogen atoms breaks off, first of all, from the hydrocarbon molecule. The radical obtained dissociates successively, just as in the gaseous phase, into olefins and lighter radicals. A new possible direction of reaction emerges in this process, a direction which was absent in homogenous cracking. Unstable radicals, capable of further disintegration in the gaseous phase, interacting with adsorbed atoms H, form saturated molecules. It follows, that on coal cracking should produce greater relative quantities of paraffins than produced through homogenous pyrolysis. At the same time, paraffins formed in the course of catalytic cracking should possess, on the average, a greater molecular weight. These conclusions correspond with experimental data 37/.

This scheme leads to the following conclusion: for each hydrocarbon molecule RH, which enters into reaction, there should be formed always one molecule of saturated hydrocarbon of a rather low-molecular weight (of the R'H type). But it follows from experiment that cracking of a number of saturated hydrocarbons (various isomeric hexanes) on coal produces approximately 150 molecules R'H per 100 molecules of RH 37/. This points to the presence of some other secondary mechanism which secures the formation of saturated hydrocarbons from olefins formed during the disintegration of the heavy radical R. That such processes do actually occur is indicated also by the large percentage of paraffins in the products of olefin cracking on coal. To the first approximation it can be assumed that the initially formed radical has approximately equal probabilities

of disintegrating into a long radical and a short olefin or, in reverse, into a short radical and a long olefin. Because the latter is cracked on coal approximately in the same way as the maximal hydrocarbons, such a process must lead to the quantity of ratio $\frac{(R'H)}{\Delta(RH)} = 1.5$, where $\Delta(RH)$ is the number of molecules of saturated hydrocarbons which have entered the reaction.

A number of peculiarities of catalytic processes (in particular, their radical character) allows one to suppose that at their basis lies a chain mechanism. But the inadequacy of our information does not permit us to conduct an analysis of this supposition that would be to any degree convincing. Accepting the applicability of concepts about chains to these reactions, it is possible to postulate the following two mechanisms: either a chain mechanism, in which a certain number of links of each cycle is materialized on the surface, or a simple chain of reactions, characteristic for vapor-phase cracking, with a heterogenous origin of chains.

The basic qualitative distinctions of processes of cracking, proceeding in conformity with ionic mechanism on so-called acidic-basic catalysts (alum-silicates and others), are: a noticeable increase in the proportion of olefins in the cracking products, a decrease in the average molecular weight of these olefins, and finally -- the presence of considerable isomerization*

These facts find the following explanation: If in cracking on coal the olefins formed in the disintegration of the radicls are capable, in their own turn, of being subjected to radical cracking, then on catalysts of the type of alum-silicates the olefins experience a totally different transformation. Supposing that on the surface of such catalysts there are free ions of hydrogen, which easily enter into reactions with double bonded compounds forming carbonium-ions 38/:

$$H^+ + RC(H) = CHR' \longrightarrow RCH_2\text{-}\overset{+}{C}HR'. \qquad (23)$$

Subsequent direction of the reaction is determined by the properties of tri-valent ion C^+.

*These conclusions follow from the analysis of data on the cracking of isomeric hexanes 37/.

If the double bond is situated in position 1 (1-butane, 1-pentane, etc.) then, in accordance with Markovnikov's rule, ion H^+ attaches itself to group CH_2 and there is formed carbonium-ion of the type

$$CH_3-\overset{+}{C}H-CH_2-\ldots \quad *$$

Such complex carbonium-ions are unstable and readily disintegrate with a transferral of the positive charge and the formation of a double bond, e.g.:

$$CH_3-\overset{+}{C}H-CH_2-CH_2-CH_2R \longrightarrow CH_3-CH = CH_2+\overset{+}{C}H_2-CH_2R. \quad (24)$$

The ion thusly-formed has two possibilities -- either to disintegrate with the formation of ethylene and an ion of R^+, or to regroup into a more stable ion as per:

$$\overset{+}{C}H_2-CH_3R \longrightarrow CH_2 = CHR+H^+ \longrightarrow CH_3-\overset{+}{C}HR \quad (25)$$

with a further disintegration along the lines of the mechanism earlier described. The relation of the rates of these two processes must be determined by the structure of radical residue R and by the properties of the catalysts. Because thermo-dynamically that ion C^+ is most stable with which the least number of atoms of hydrogen is connected, it is to be expected that carbonium-ions with a great number of atoms C will isomerize, forming ions of the type

$$R-\overset{+}{\underset{\displaystyle R'}{\underset{|}{C}}}-R''$$

The mechanism of formation of a carbonium-ion of iso-structure may be visualized in the following manner:

$$H^+ + CH_2 = CH-CH_2-CH_3 \longrightarrow CH_3-\overset{+}{C}H-CH_2-CH_3 \longrightarrow CH_3-CH=CH_2 +$$

$$+ \overset{+}{C}H_3 \longrightarrow CH_2-\overset{+}{\underset{\displaystyle CH_3}{\underset{|}{C}}}H-CH_3 \longrightarrow CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3+H^+ \longrightarrow CH_3-\overset{+}{\underset{\displaystyle CH_3}{\underset{|}{C}}}-CH_3. \quad (26)$$

*It is demonstrated by direct computation 39/, that the energy of affinity of the proton to atoms of C in compounds: $H_2C=CH_2$; $H_2C=CHCH_3$; $H_2C=CCH_3CH_3$ are correspondingly equal: 152 and 152; 175.5 and 168.5; 189 and 168 Kcal.

The final act of the disintegration process and of isomerization of the olefin lies in the return of ione H^+ to the catalyst, with the formation of a unsaturated compound.

All of the foregoing indicates that the olefin, formed through disintegration of the primary radical in ionic catalytic cracking, is cracked further with the formation of either olefine of small weight, or of isomeric olefins, and the formation of saturated hydrocarbons occurs in olefin disintegration, apparently, very seldom. From this it follows, in particular, that in accordance with experimental findings 37/ these processes have $\frac{(R'H)}{\Delta(RH)} \approx 1$.

It must be noted that in the presence of ions H^+, CH_3 etc., also possible are processes of inner regrouping and isomerization of radicals, which lead to the formation of more stable radicals, such as,

$$-CH_2-CH_2-CH_2-R + H^+ \longrightarrow CH_3-\underset{|}{CH}-CH_2-R + H^+ \qquad (27)$$

$$CH_3-\underset{|}{CH}-CH_2-R + \overset{+}{C}H_3 \longrightarrow CH_3-\underset{|}{\overset{CH_3}{\overset{|}{C}}}-CH_2-R + H^+ \qquad (28)$$

These processes allow us to explain the emergence in ionic cracking, of considerable quantities of isoparaffins.

The following summation can be made of the foregoing examination of the processes of vapor-phase and catalytic cracking. In the gaseous phase the process has a chain character, the origin of chains occurring with a rupture in the C-C connection bond.* The break-up of the skeleton is realized by way of the disintegration of the radical with the formation of olefins. The continuation of the chain and the appearance of paraffins occurs when the radical breaks off an atom H from the molecule of the initial substance.

In radical catalytic cracking the primary act consists in the break-off of atom H from the molecule, followed by the disintegration of the radical, just as

*See note to page 687.

in the gaseous phase, limited by the possibility of saturation of the radical by way of incorporating one of the atoms H, adsorbed on the surface.

In the case of ionic catalytic cracking the first act remains the same as in the case of radical cracking, but due to a great concentration of free ions on the surface, both olefins and radicals are capable of becoming subject to isomerization. In addition, the further disintegration of olefins is considerably facilitated in this case.

In both instances of catalytic cracking, the chain character of the process remains possible, this being determined by interrelation of speeds of the process

$$R' + RH = R'H + R$$

and of the reaction of interaction of R' with atom H chemisorbed on the surface.

III. Termination of Chains

As a result of reactions with the participation of free radicals, such low-activity compounds are formed that their further transformation does not lead to the regeneration of the active radical. The development of the reaction chain is thus terminated. Reactions of this kind are called reaction of disruption of chains.

As was pointed out earlier, free valency cannot disappear in the reaction of a radical with a saturated molecule. Therefore a reaction of chain disruption must be either the recombination of two radicals or the formation of low-activity radical, which, despite the availability of free valency, is not capable of entering into reaction of chain continuation.

It must be noted that the concept of activity on the part of a radical is relative and is determined by chemical properties of that system in which the given radicals are formed. Thus, for instance, the formation of radical CCl_3 in the oxidation of hydrogen in the presence of CCl_4 leads to the termination of the chain, because it cannot enter into the reaction of chain propagation with H_2 or O_2. But in photochemical polymerization of a number of paraffins, the same radicals CCl_3, entering into reaction with a monomer, continue the chains 9/.

Let us first examine reactions of the interaction between two active particles (radicals or atoms). In the double-collision of two atoms (e.g., H+H) the formation of a stable molecule is highly improbable. The whole energy of reaction (for hydrogen -- 102.7 kilogram-calories/molecules) will be concentrated mainly in one vibrational degree of freedom, and the newly-formed molecule (quasi-molecule) again dissociates into atoms. Stabilization of the quasi-molecule is possible only in that case when during the period of its existence ($\sim 10^{-12}$ seconds) it succeeds in transferring its excess energy to some other molecule. In other words, this means that a recombination of two atoms can occur only in the case of triple inter-collisions of the type

$$A + A + M = A_2 + M, \qquad (29)$$

where M -- any particle.

The correctness of this supposition was proven by experiments on measuring the effect of general pressure and of additions of various gases on the speed of recombination 40, 41/.

The efficacy of various molecules in the function of the third body in reaction (29) depends on their physico-chemical properties and on the number of degrees of freedom, capable of participating in the redistribution of energy of recombination. Thus, for instance, it was demonstrated through direct experiments41/ that in the case of recombination of bromine atoms the effectiveness of molecules C_6H_6, CO_2, CH_4, N_2, H_2 and of atoms He are related as 60:10:7:4.5:2:1. The stabilizing ability of biatomic molecules and of atoms of inert gases (H_2, N_2, O_2, He, Ar) is definitively [odnoznachno ?] determined through their masses and through their effective gaseous kinetic cross-section 17/.

When collision of two more complex radical (e.g. CH_3, C_2H_5, etc.) occurs, energy of reaction can redistribute itself on various degrees of freedom, which sometimes leads to stabilization of newly-formed molecules even in the absence of the third particle*:

*Apparently, stabilization of the quasi-molecule occurs especially well on the wall which facilitates the draining of energy (see 34/, page 18).

$$C_2H_5 + C_2H_5 = C_4H_{10} \qquad (30)$$

Increased energy-content in the quasi-molecule can sometimes lead to a different reaction, the so-called reaction of disproportionation:

$$CH_3\text{-}CH_2\text{-} + \text{-}CH_2\text{-}CH_3 \longrightarrow CH_3\text{-}CH_3 + CH_2 = CH_2, \quad (31)$$

as a result of which two stable molecules are formed, one of which possesses a double bond. Interrelationship between speeds of reactions (30) and (31) is determined by the structure of interacting radicals, energy of reaction and by the degree of complexity of the molecule being formed. Thus, for instance, in the case of recombination of n-butyl radicals, emerging in the photochemical hydrogenation of butane, the reaction of disproportionation (31)

$$2n\text{-}C_4H_9 \longrightarrow C_4H_8 + C_4H_{10}$$

proceeds merely half as fast as the reaction of dimerization 26/ of reaction (30)

$$2n\text{-}C_4H_9 \longrightarrow C_8H_{18}.$$

But in the case of isobutyl radicals only isobutyl is formed almost exclusively.

The dimerization of the allyl radical

$$2CH_2 = CH\text{-}CH_2\text{-} \longrightarrow CH_2 = CH\text{-}CH_2\text{-}CH_2\text{-}CH = CH_2,$$

in the course of which considerably less energy is given off than in the reaction of two allyl radicals (as, e.g., (30)), proceeds also without any practically discernible disproportionation (see 26/, pages 346-348, 174.).

The above mechanism of reaction of disproportionation (31) is based on the acceptance of transfer of atom H in a complex molecule into the β-position (see also page 686). This assumption appears more general than the usual scheme

$$CH_3\text{-}CH_2\text{-} + CH_3\text{-}CH_2\text{-} \longrightarrow CH_3\text{-}CH_3 + CH_2 = CH_2 \quad (31')$$

because in the case of more complex reactions of this type, e.g., in the case of interaction of propylic radicals, the usual scheme (31') requires the breaking off

of two bonds of C-H with the transfer of atoms H to neighboring atoms C, while mechanism (31) allows an explanation of the passage of the reaction with the aid of the breaking of only one bond C-H.

Analysis of experimental data leads to the same conclusion. The data used is on electro-chemical synthesis of hydrocarbons from partially deuterized butyric acid $CH_3CH_2CD_2COOH$ 33/. Distribution of atoms D in molecules of propane and propylene, obtained through the reaction of disproportionation, which takes place according to analysis findings, as per the equation:

$$2CH_3-CH_2-CD_2 \longrightarrow CH_3-CH = CD_2 + CH_3-CH_2-CD_2H,$$

points to the correctness of the earlier-stated assumption [that if one proceeds from scheme (31'), then propylene should represent a mixture of $CH_3-CH = CD_2$ and $CH_2 = CH-CD_2H$], [preceding brackets in original text].

All three examined reactions (29), (30), and (31) represent processes connected with the mutual compensation of free valencies of two interacting radicals. The speed of these processes, which lead to the disruption of two chains of reaction, is proportional to the second degree of concentration of active particles (quadratic disruption).

Calculation of reactions of such kind, when examining the mechanism of chain processes, proves to be fully sufficient in a number of cases for the purpose of explaining all of the kinetic regularities of these reactions as observable in experiments. The common indication which points at the substantial role of reactions of quadratic disruption in a process under examination lies in the proportionality of the speed of reactions to the square root of speed of chain formation (in the case of artificial initiation of chains) or to the square root of concentration of one of primary substances (in thermal reaction).

However, the above-stated pertains to unramified chain reactions only, or-in the case of ramified chains-- to such values of p and T which lie a sufficient distance from the values for chain ignition.

The rather sharp transformation, while p and T change negligibly, from stationary slow reaction to isothermic ignition -- characteristic for reactions with ramified chains -- cannot be explained on the basis of the proposition that the chains suffer a

quadratic disruption. The critical character of these phenomena was successfully interpreted only on the basis of a concept of reaction of chain termination, flowing along the lines of the first order-with respect to concentration of free radicals* Termination reactions of the first order can proceed in homogenous environment [medium] as well as on the wall.

Termination of a chain in case of reactions in a volume is observed, as was noted earlier, when the reaction of an active reaction-capable particle forms a low-activity radical. The speed of formation of such radicals does indeed determine the length of reaction chains.

A number of substances, called inhibitors, interact especially readily with free radicals and, because it follows from a large body of data pertaining to the most diverse reactions that the faster the reaction of radical with molecule the less active is the new radical thereby forming, the addition of such substances can quite considerably hamper the reaction.

As an example, let us examine the action of molecular iodine on the chain ignition of hydrogen with oxygen 17/. It is sufficient to add several thousandths of one percent of iodine to the mixture H_2+O_2 in order to displace the area of ignition by several tens of degrees in the direction of high temperatures. This shows that a minute addition of an inhibiting substance can fully supress a reaction which occurs practically instantaneously in the absence of the inhibitor. Such a strong action on the part of the inhibitor becomes understandable, if we take into consideration, that the rate constant of the basic process into which atoms of H enter in the case of oxidation of a pure mixture $H+O_2 = OH+O$, under the conditions of experiment ($T=500^\circ$) is 10^5 times smaller than the rate constant of reaction $H + I_2 = HI+I$, and that reactiveness of atoms of I is considerably below that of radical OH and atom O (the constant of speeds of reactions

$$I + H_2 = HI + H,\ O + H_2 = OH+H \text{ and } OH+H_2 = H_2O+H$$

are correspondingly in a ratio, as $1:1.3\times10^6:1.\times10^7$).

The same braking action upon the oxidation of hydrogen is also exerted by various hydrocarbons.

*See 19/, page 110.

However, because the speed of processes of the type $H + RH = R + H_2$ is many times smaller than that of reaction $H + I_2 = HI + I$, it is necessary to employ larger additions of these substances (of the order of 0.1-1%) in order to obtain significant effects. Effectiveness of braking depends, in this case as well, on two factors relative rate of the reaction $H + RH = R + H_2$ and on the reactiveness of radical R.

Disruption can be effective only if radical R is considerably more inert than the corresponding particle that comes into existence through reaction in a primary pure mixture.

As a graphic example of the fact that effectiveness of inhibition is determined by the activity of the radical (obtained with the participation of the inhibitor molecule) we can take the earlier-stated comparison (page 686) between the effectiveness of isobutane and propylene in the capacity of inhibitors of complex processes. Although speeds of radicals formation

$$-CH_2-\dot{C}H = CH_2 \text{ and } CH_3-\dot{C}(CH_3)-CH_3$$

are approximately identical, the first one is considerably more inert (due to a double bond). It is precisely because of this that propylene inhibits chain reactions much more than isobutane.

Very often, especially at low pressures, the termination of reaction chains in a homogenous environment occurs as a result of heterogenous reactions of atoms and radicals. The speed of these reactions is characterized, in the general instance, by the effectiveness of interaction of the atom (or radical) with the surface* and by conditions of diffusion of active particles towards the wall. When values of ε are small, termination of chains is limited to the chemical stage (kinetic area); at great values of ε -- to diffusion (area of diffusion). It is obvious in the second case that the effective speed of chain termination, equal to the speed of diffusion of atoms towards the surface, will be

*The following ratio is called effectiveness of interaction of atom with the surface:

$$\varepsilon = \frac{\text{the number of collisions of atom with surface, lead-to reaction.}}{\text{the total number of collisions of the atom with surface.}}$$

proportional to the first degree of concentration of active particles. Kinetic investigation of complex chain reactions at low pressures, as well as direct study of kinetics of interaction of free atoms with various surfaces, indicate that at small ε, also, an identical dependence on concentration is found 42/.

A most detailed investigation has been made of the problem of recombination of atoms of hydrogen on diverse surfaces. It was established that the mechanism of this process consists of the following elementary stages*:

$$H + \text{wall} \longrightarrow H_{ads.}$$

$$H + H_{ads.} \longrightarrow H_{2ads.} \longrightarrow H_2.$$

The value of ε for atoms of H lies within the limits from 10^{-5} to 1. The probability of recombination of atoms H is very great on Pt, Fe, Ag and a number of oxides $ZnO.Cr_2O_3$, M_oO_3, PbO etc., 17, 42/. Very small values of ε_H are characteristic for freshly fused glass, glass and quartz, rinsed [promytyy?] $K_2B_4O_7$, and for M_2O. It is necessary to note that solely pure recombination is not always observable in cases of the interaction of atoms on the surface. Thus, when atoms H interact with MoO_3, the quantity of activity of the surface increases in the course of the experiment (whereby MoO_3 is partially transformed into MoO_2), and then the surface becomes stabilized and the speed of reaction remains constant. In other instances (PbO, ZnO) the surface changes constantly under the action of atoms, and oxide is first restored to metal, and the latter reacts with formation of hydrides. Effect of atoms H on coal produces hydrocarbons 45/.

It is interesting to note here that practically all surfaces, which possess large (Pt and other metals, ZnO, Cr_2O_3, MoO_3-MoO_2, etc.) are also catalysts of hydration and dehydration. On the other hand, ε_H is not large on cracking catalysts (coal and alumo-silicates). In

*This mechanism is confirmed by direct experiments, which show that adsorption of hydrogen atoms on glass is, in some conditions, irreversible and that the stationary speed of recombination is determined as much faster in repeated experiments.

such manner arises the possibility of comparison between cracking and hydrogenation and dehydrogenation properties of catalysts through the extent of the effectiveness of recombination of hydrogen atoms. Furthermore, since the recombination of atoms is a radical reaction, on the basis on the earlier-noted parallelism the conclusion suggests itself that the question of the possibility of chain mechanism of some heterogenous catalytic reactions can be solved precisely by way of study of heterogenous reactions of free atoms and radicals.

In summing up the above-stated comments about reactions of chain disruption in the first and second orders, the following must be noted.

The proportionality of the rate to the square root of concentration of initial substances or of rate of initiation in complex reactions points to the dominant role of quadratic disruption. Absence of such a dependence, and also the presence of isothermic ignition (in the case of ramified chains) indicates termination via the first order.

But detailed studies of ignition show that termination via the first order is too slow for an explanation of the kinetics of accumulation of intermediate products. Semenov demonstrated 43/, on the basis of a theoretical analysis of Koval'skiy's experimental data, that within the ignition area -- when the concentration of active particles reaches very large values -- the reactions of quadratic disruption again enter into force.

A very important practical significance is held by reactions of chain disruption in the examination of the problem of the possibility of spreading of the flame under various conditions. No exact chemical theory of these phenomena has been created up till now. It is known that a number of substances, called phlegmatizators (CCl_4, $SnCl_4$, $C_2H_4Cl_2$ and others), decrease the speed of the flame or make its spreading completely impossible. Presence of dust in gaseous mixture, and in some cases -- of specially powdered particles of various salts (in the main, halogen compounds of alkali and alkali-earth metals) often leads to the same effect 44/.

Because the phenomenon of flame-spreading is conditioned by chemical reaction of burning and also because phlegmatizers are very close in their chemical properties to inhibitors of oxidation reactions, and the phlegmatizing action of various films and dusts is closely connected with their effectiveness with

respect to the recombination of active particles (atoms H and radicals OH, CH_3, etc.), we have all the reason to suppose that the action of all these substances on flame-spreading is connected with the annihilation of active centers.

Material presented in this article does not, by far, embrace all of the available in literature data about the chemical properties of free radicals. A detailed treatment of this problem is impossible within the limited boundaries of an article for a journal. Therefore we were forced to make use of only those works which have a direct bearing upon the basic questions discussed in this article. When selecting these key-questions we endeavored to put in relief those peculiarities of the chain theory, which until now had been discussed in literature without sufficient detail. Because of this, we did not at all touch upon a large group of works devoted to reactions of atoms O and H and radicals OH with various molecules, the results of which are well known to the Soviet reader (works by Avramenko, Kondrat'yev and others). But even in the method of presentation worked out by us -- classification of elementary reactions not according to their chemistry [khemizm ?], but according to their part in the chain process, it of course remained still impossible to present within the narrow frame of the article a detailed and strictly logically consistent picture of the courses of all of the basic chain processes. We devoted primary attention to questions which are being discussed for the first time, or requiring -- in our opinion -- a reexamination. It must be stressed that it is precisely those questions which are at the present most controversial, and if in some cases our argumentations may be regarded as not fully convincing, then in a number of other instances the stated suppositions are hypothetical and must be either confirmed or debunked in the course of subsequent investigations.

Such a structure of the article permits us to hope that, not being a simple review, it will prove beneficial from the view point of a correct and goal-oriented formulation of chemical experimentation, and in that manner will facilitate further fruitful development of one of the most captivating chapters of chemical science.

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